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On

Para chlor meta sulpho benzoic acid.

and

some of its derivatives.

A Dissertation

presented to the Board of University

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Para-chlor-meta-sulpho-benzoic acid

Para-chlor-benzoic acid.

Occurrence in Commercial Saccharine.

My attention was directed to p.chlor-benzoic acid by observing its occurrence in commercial saccharin. In the preparation of o-sulpho-benzoic acid from the benzoic sulphinide contained in saccharin, the saccharin is boiled for several hours with dilute hydrochloric acid in a flask connected with a reflux condenser; the benzoic sulphinide is thus converted into the acid ammonium salt of o-sulpho-benzoic acid which is soluble in water, the p-sulphamin-benzoic acid originally contained in the saccharin remains as such and is insoluble in cold water.(1)

(1) Remsen and Dohme. Am. Ch. Jr. XI. 332.

During this operation there is formed a volatile product which condenses in white flocculent masses, and is returned with the condensed water vapour and is insoluble in cold water. After the operation has been completed the contents of the flask are allowed to cool, the soluble acid ammonium salt of o-sulpho-benzoic acid is filtered off. The volatile white flocculent substance which proved to be p-chlor-benzoic acid can be recovered from the insoluble residues by distillation with steam, when by it passes over and can be collected in almost pure condition. It is very difficultly soluble in cold water and can be purified without loss by dissolving it in a solution of sodium carbonate and reprecipitating with sulphuric acid. It can be distilled with steam directly out of Saccharin by the addition of a

mineral acid to the Saccharine. The distillate of p-chlor-benzoic acid causes immediately on the neutralization of the free acid. The yield is not affected by using a concentrated solution of the mineral acid, nor by treating the Saccharine in successive small portions. Para-chlor-benzoic acid is therefore in all probability present in Saccharine in the form of a salt and is freed from the base by the addition of the mineral acid. From one specimen of Saccharine no p-chlor-benzoic acid could be obtained.

In the methods of analysis hitherto devised for the determination of the benzoic sulphinide, and the impurities contained in Saccharine, the presence of p-chlor-benzoic acid as an impurity has not been regarded. According to the method of Remsen & Burton (1) which

(1) Am. Ch. J. XI 401

is based on the quantitative conversion of the sulphinide into o-sulpho-benzoic acid, the p-chlor-benzoic acid is found from its base, and is estimated along with the p-sulphamine-benzoic acid as an impurity. If it were desired to make a special determination of the p-chlor--benzoic acid, it would only be necessary to modify this method by distilling the p-chlor-benzoic acid away from the p-sulphamine-benzoic acid and weighing each separately.

In the method of Falkowski no acid is used, the p-chlor-benzoic acid remains combined with its base as a soluble salt, and is estimated, along with all substances which are more soluble than p-sulphamine-benzoic acid, as benzoic sulphinide.

The presence of a salt of p-chlor--benzoic acid will explain the occurrence

of chlorine in the ash of Saccharin as has been determined by S. Hirschfeld[1]

[Note: Hirschfeld has again used the empirical method devised by Falkowski for the analysis of Saccharin, after we exact a method as that of Remsen & Burton (Am. Ch. Jr XI, 403) has been devised. I have had occasion to prepare pure benzoic sulphinide out of commercial Saccharin and from personal experience and the experience of many others, I know that no reliance whatsoever is to be placed in the method of Falkowski which depends on the supposition, that benzoic sulphinide and para-sulphamine-benzoic acid can be separated by three fractional crystallizations in water, and that the resulting mother-liquors upon evaporation give approximately pure benzoic sulphinide. Hirschfeld confirms the

[1] Arch: Ein Beitrag zur Saccharinfrage. Erlangen 1891.

erroneous statement of Salkowski that benzoic sulphinide after long continued boiling with dilute hydrochloric acid is left unchanged. (See Remsen and Burton: On the action of dilute acids on benzoic sulphinide and the analysis of commercial Saccharin. Am. Ch. Jr. XI, 403; also Remsen and Dohme Am. Ch. Jr XI. 332.). The various connections in which Professor Ira Remsen's name is used in this thesis by Hirschfeld can be ascribed only to ~~an unfortunate~~ ignorance of the literature on the subject treated of.]

The volatility with water-vapour of p-chlor-benzoic acid has not hitherto been recorded. The m-chlor-benzoic acid and the o-chlor-benzoic acid are not volatile with water vapour. Beilstein and Kuhlberg[1] found that the dichlorbenzoic

(1) Ann. CLII, 226.

acid in which one of the chlorine atoms is in the para position relative to the carboxyl group, is volatile with water vapour. So far as these observations go, it would seem that the volatility with water vapour of chlor substitution products of benzoic acid is in some way dependent on the para position of the chlorine.

The p-chlor-benzoic acid obtained from commercial Saccharin agreed in all respects with the descriptions given by Beilstein and Geitner,[1] and by Emmerling,[2] and with p-chlor-benzoic acid which I prepared later on from p-chlor-toluene. It is precipitated by acids from its soluble sodium salt in white flocculent masses, and sublimes in needles, which melt at 234°. The Calcium salt crystallizes in efflorescent forms with nine molecules of water of

(1) Ann. CXXXIX, 335.
(2) Ber. VIII, 550

crystallization."[1] Analyses of the calcium salt resulted as follows:

I. .2584 gram salt gave .0874 gram $CaSO_4$ = .0252 gram Ca.

II .2189 gram salt gave .0730 gram $CaSO_4$ = .0215 gram Ca.

	Calculated for $(C_6H_4ClCO)_2Ca + 3H_2O$	Found. I	II
Ca	9.89	9.92	9.81

The identity of the p-chlorbenzoic acid obtained from commercial Saccharine is thus fully confirmed.

[1] W. Beilstein and Geitner, Ann CXXXIX, 336.

Para-chlor-benzoic acid from p.-Sulphamine-benzoic acid.

For a supply of p-chlor-benzoic acid to be utilized in a reinvestigation of its sulphonic acid derivative it was found necessary to cast about for a method of preparation other than the oxidation from Saccharin. It was supposed that by treating p.-sulphamine-benzoic acid with an excess of phosphorus pentachloride at an high temperature, the sulphonamide group would be driven out and replaced by chlorine, thus:

$$C_6H_4\begin{cases}COOH\ (1)\\ SO_2NH_2\ (4)\end{cases} + PCl_5 = C_6H_4\begin{cases}COCl\ (1)\\ Cl\ (4)\end{cases} + POCl_3 + X.$$

Then upon saponifying the resulting p-chlor-benzoyl chloride it would be transformed into

p.-chlor-benzoic acid and could then be distilled with steam from the accompanying impurities. This reaction has been successful with many sulphonic acids; a case bearing closely on the experiment in question is the conversion of di-chlor-para-sulpho-benzoic acid into tri-chlor-benzoic acid accomplished by R. Otto.[1] In the case of a sulphamine-benzoic acid the action of phosphorus pentachloride might be to form p.-chlor-benzonitrile, analagous to the formation of o.-chlor-benzo-nitrile from benzoic sulphinide and phosphorus pentachloride.[2] Both of these suppositions were realized but the yield of p.-chlor-benzoic acid was too small to recommend the use of this method as a practicable one for the preparation of the acid in quantity. The experiments are here given in more detail.

(1) Ann. CXXIII, 226
(2) Remsen and Saltar. Am. Ch. Jr XI, 332.

Experiment I.

Ten grams of dry powdered p-sulphamine-benzoic acid are mixed in a retort with twenty one grams of phosphorus pentachloride — which is equivalent to two molecules of phosphorus pentachloride to one molecule of p-sulphamine-benzoic acid. The retort is placed in a sulphuric acid bath and the temperature is gradually raised. At 100° action takes place. The temperature is raised to 140° to get rid of all phosphorus oxychloride. The contents of the retort are then distilled with steam. A small yield of p-chlor-benzoic acid is distilled over. The first portions of the distillate have an odour very much like that of benzonitrile. Any p-chlor-benzo-nitrile formed in this experiment would have been found in the distillate since it is volatile with steam.

Experiment II. Another portion of ten grams of

p-sulphamine-benzoic acid is treated as in Experiment I with the exception that the temperature is raised to 220°. With the last portions of the phosphorous oxychloride there passes over an oily substance which solidifies under water in a white crystalline mass, with a melting point at 99°. It was identified as para-chlor-benzonitrile by converting it with caustic potash into para-chlor-benzoic acid. The contents of the retort are treated as in Experiment I and again a small yield of p-chlor-benzoic acid is obtained.

Experiment III. Eight grams of p-sulphamine-benzoic acid are treated with thirty-four grams of phosphorous pentachloride - equivalent to four molecules of the pentachloride to one of the acid. One half of this mixture is heated to 135°, and the other half to 190°. Neither of them gives a satisfactory yield of p-chlor-benzoic

acid.

It was observed that the greatest yield of p-chlor-benzonitrile was obtained at the highest temperature employed - that is 220° in Experiment II the temperature was 220°. To determine the effect of heat alone on p-sulphamine-benzoic acid, a portion was distilled at a high temperature in an oil-bath. This yielded an oily distillate which was identified as benzonitrile by boiling it with water whereby it was transformed into benzoic acid which melted at 119°. The contents of the retort also contained some benzonitrile. The yield of benzonitrile was only slightly increased by repeating the experiment with the addition of phosphorus pentoxide to the p-sulphamine-benzoic acid. No experiments were tried as to the result of heating p-sulphamine-benzoic acid alone or with phosphorus pentachloride

in sealed tubes under pressure.

Para-chlor-benzoic acid from p-chlor-toluene.

While the experiments described above were in progress, other experiments were being carried on with Emmerling's method for the preparation of p-chlor-benzoic acid.[1] By this method small quantities of p-chlor-toluene are treated with dilute solutions of potassium permanganate, containing one part of permanganate to three parts of p-chlor-toluene used. Taking into account that ordinary p-chlor-toluene usually contains from 25 to twenty five to fifty per cent. of o-chlor-toluene and that for a complete decoloration of the dilute permanganate solution about nine hours are necessary, this method is not more rapid than the one above described for getting p-chlor-

1) Ber. III. 680.

-benzoic acid out of p-oxyphenamine-benzoic acid. But it was found that concentrated solutions of potassium permanganate such as exist in p-oxy-toluic acid mixt. in every way comparable to the results obtained by the use of dilute solutions of potassium permanganate. The following method, in all essentials like that of Immerling, is the best one available for the preparation of p-oxybenzoic acid: Into a four liter globe flask containing three liters of distilled water are put one hundred and fifty grams of potassium permanganate. To this is added fifty to seventy cubic centimeters of p-oxy-toluene. The flask is placed in a bath of boiling water, & is connected with a reflux condenser. After having been kept at the temperature of boiling water for twelve to fifteen hours the permanganate color disappears from the solution and there is

left in the flask — unoxidized p-chlor-toluene and o.chlor-toluene, insoluble manganese superhydrate and the soluble potassium salts of para and ortho-chlor-benzoic acid. The excess of p-chlor-toluene is readily recovered by distillation with steam. While still hot the soluble salts of para and ortho-chlor benzoic acid are filtered from the insoluble manganese superhydrate. The solution of potassium para and ortho-chlor-benzoate is allowed to cool and is then treated with sulphuric acid, whereby the para-chlor-benzoic acid is completely precipitated together with a little o-chlorbenzoic acid. The greater part of the o-chlor-benzoic acid remaining in solution is filtered from the insoluble portion. The p-chlor-benzoic acid is rendered totally free from o-chlor-benzoic acid by washing two or three times with a

little hot water. The ochlor-benzoic acid can be recovered from the filtrate by evaporation with boiling (in nearly pure condition). It still contains a little p-chlor-benzoic acid which is gotten rid of by distilling it out with steam, or more simply by repeatedly dampening the impure ochlor-benzoic acid with water & placing it in an air-bath at 120°. After two or three such operations the ortho-chlor-benzoic acid is also free from all p-chlor-benzoic acid.

The mixed oxides of p-chlor-toluene and ortho-chlor-toluene is again treated as above. In thus treating the mixed oxides of para- and ortho-chlor-toluene no marked change in the ratios of p-chlor-benzoic acid to ortho-chlor-benzoic acid obtained was observed, and it is probable that the oxidation of p-chlor-toluene and o-chlor-toluene by potassium permanganate goes on with about the same

rapidity. Para-chlor-benzoic acid by treatment with sulphuric anhydride gives p-chlor-meta-sulpho-benzoic acid.

Para-chlor-meta-sulpho-benz- acid.

This acid has been investigated by Th Cöllen and C. Böttinger.(#) They described methods of preparation from p-chlor-benzoic acid by treating it with sulphuric anhydride, or with fuming sulphuric acid containing ninety percent of sulphuric anhydride.

The following compounds are described by them:

Barium salt, crystallizing in tablets with three molecules of water of crystallization;

Lead salt, crystallizing in rhombic tablets with four molecules of water of crystallization;

Copper salt, crystallizing in blue needles with six molecules of water of crystallization;

(#) Ber. 12 [illegible]

Acid potassium salt, crystallizing in fine needles;

Neutral potassium salt, crystallizing in quartz like forms;

Acid sodium salt, crystallizing in needles with two molecules of water of crystallization;

Magnesium salt, crystallizing in branched needles with six molecules of water of crystallization;

Zinc salt, crystallizing in long needles with four molecules of water of crystallization;

Neutral Silver salt, crystallizing in flakes with one molecule of water of crystallization;

Free acid, crystallizing in needles with three molecules of water of crystallization.

In attempts to determine the position of the sulphonic acid group they employed the following methods: Reduction of the free acid with sodium-amalgam in the expectation

of replacing the para-chlorine atom by hydrogen and thereby converting the acid into a known sulpho-benzoic acid; fusion of the potassium salt with caustic potash and silver oxide in order to obtain a di-hydroxy-benzoic acid; fusion of the potassium salt with sodium formate in the hope of obtaining mono, di, and tri-carbonic acids of benzene. From these attempts no conclusion was reached as to the constitution of the acid, which will be shown to be *p*-chlor-*m*-sulpho-benzoic acid.

By treatment of the sodium salt with phosphorus pentachloride, this yielded a mixture of chlorides to which the formulæ, $C_6H_2\begin{cases}Cl\\COOH\\SO_2Cl\end{cases}$ and $C_6H_3\begin{cases}Cl\\COCl\\SO_2OH\end{cases}$ were ascribed. It will be shown that the dichloride, $C_6H_3\begin{cases}Cl\\COCl\\SO_2Cl\end{cases}$

is obtained by this reaction.

By successive treatment of the sodium salt with phosphorus pentachloride and ammonia, they obtained what was described as an amidammonium salt and to which they gave the formula, $C_6H_3Cl\begin{matrix}SO_2ONH_4,NH_2\\CO\end{matrix}$. It will be shown that these reactions lead to the diamide, $C_6H_3\begin{cases}Cl\\CONH_2\\SO_2NH_2\end{cases}$.

Para-chlor-meta-sulpho-benzoic acid from para-chlor-benzoic acid.

Although Cöchen and Zöttinger prepared to convert p-chlor-benzoic acid into it sulphonic acid derivative by the use of fuming sulphuric acid containing ninety per cent of sulphuric anhydride, I have found the reaction with sulphuric anhydride alone more satisfactory. An attempt to prepare the sulphonic acid

derivative by first converting the
p-chlor-benzoic acid into p-chlor-benzoyl
chloride, and then treating with fuming
sulphuric acid, or with fuming sulphuric acid
and sulphuric anhydride was not as
successful. After standing four days the
mass still showed a precipitate of p-chlor-
-benzoic acid upon being treated with water
and boiled. The method adopted as the
most practicable is the following one:
Into a receiver is placed dry, powdered
p-chlor-benzoic acid, and into it is
distilled sulphuric anhydride from
a retort containing fuming sulphuric
acid. A brownish viscous mass is
formed. By occasionally heating this
mass to the boiling-point of the sulphuric
anhydride, the reaction is hastened and
is fully completed in the course of a day.

The contents of the receiver are now transferred to a retort and the excess of sulphonic anhydride is distilled off. The para-chlor-sulpho-benzoic acid thus formed is poured into water and dissolves completely. The solution is boiled with barium carbonate to get rid of the excess of sulphuric acid. The filtrate from the barium sulphate gives excellent crystals of barium p-chlor-m-sulpho-benzoate on concentration. Barium p-chlorm-sulpho-benzoate is difficultly soluble in cold water. The final mother liquors from the crystallizations of the barium salt of p-chlor-m-sulphobenzoic acid contained a much more soluble barium salt. This more soluble salt is not the salt of p-chlor-o-sulpho benzoic acid as was found by Caspari the free acid and some of its derivatives with the substances

obtained by J. J. De Raade from p-chlor-toluene-ortho-disulphonic acid.[1]

It is therefore, in all probability, the barium salt of a p-chlor-di-sulpho-benzoic acid.

The acid obtained in this way is by exactly precipitating the barium in barium p-chlor-m-disulpho-benzoate with sulphuric acid, crystallized from water in long needles. It is very soluble in water. An analysis of the acid gave the following results:

.2671 gram acid heated to constant weight at 150° lost .0492 gram H_2O.

gram acid gave by Carius method[#]

.1505 gram acid gave .1004 gram $BaSO_4$ = .0138 gram S

.1225 gram acid gave .0609 gram AgCl = .0151 gram Cl

	Calculated for $C_6H_3\begin{cases}Cl\\SO_3H+3H_2O\\CO_2H\end{cases}$	Found
H_2O.	18.57	18.42
S.	11.04	11.24
Cl.	12.21	12.29

[1] Ber. . Some analogous substitution products of benzene hexachloride. Johns Hopkins University 1890.

[#] These determinations of S and Cl were made by Mr. Hartman.

Salts of p-chlor-meta-sulpho-benzoic acid.

The copper, sodium, potassium, lead and zinc salts were made and were found to agree with the description given by Cöllen and Böttinger of these salts (see pages 18 and 19). The acid lead salt was prepared in the usual way. A portion of the free acid was dissolved in a known quantity of water, and this solution divided into two equal parts one of which was neutralized with lead carbonate, and subsequently treated with the other part. Upon slow concentration of the solution the acid lead salt separates in long fine needles with four molecules of water of crystallization. The

copper, lead and acid lead salts have a strong tendency toward the formation of insoluble basic salts. When the solutions were concentrated on a water-bath, even at a comparatively low temperature the basic salts separated out. This was most marked in the case of the copper salt. To obtain good crystallizations of the neutral salts, it was necessary to let the water evaporate slowly in a desiccator. A determination of the water of crystallization in the acid lead salt gave the following result:

.2852 gram acid Pb salt heated to constant weight at 160° lost .0333 gram.

	Calculated for $\left(C_6H_3\begin{cases}CC\\SO_3\\CO_2\end{cases}H\right)_2Pb + 5H_2O$	Found
H_2O	11.72	11.67

Barium salt.

The barium salt is remarkably dimorphous. It crystallized in two forms, a compact tabular form and a yielding spongy efflorescent form, both containing three molecules of water of crystallization, and under the same conditions losing it equally. The appearance of the spongy form when dried between folds of filter paper is best described by comparing it to the ordinary sea-sponge. The compact tabular form is the one which was most commonly obtained. Both forms sometimes occurred together in the same solution and, by redissolving one form, the other form could be made to crystallize out under the proper conditions. The conditions for the efflorescent form were found to be; a slow crystallization from a saturated solution at a low temperature.

IX was usually obtained by allowing a solution saturated at about 18° to stand over night during the winter months when the temperature of the laboratory would fall to about 5° during the night. IX was sometimes formed by exposing a beaker containing a saturated solution to the influence of the lower temperature out of doors, the beaker being covered by a large crystallizing disk to prevent a too sudden chilling of the solution. The arborescent form discolors readily in a little lukewarm water, the tabular form can even be fairly powdered in much more slowly discolored. Both forms contain five molecules of water of crystallization which are lost at 170°.

Analyses of these salts gave the following results:

I. .4365 gram tabular Ba salt heated at 180° to constant weight lost .0554 gram

II. .1918 gram arborescent Ba salt dried at 190° to constant weight lost .0244 gram

III. .4365 gram tabular Ba salt gave .2385 gram $BaSO_4$ = gram Ba.

IV .3128 gram tabular Ba salt gave .1711 gram $BaSO_4$ = gram Ba

	Calculated for: $C_6H_2\begin{cases}Cl\\ClO\\SO_2O\end{cases}>Ba + 3H_2O$	Found. Tabular	Arborescent:
H_2O	12.69	12.68	12.72
Ba	32.23	32.15 32.18	——

It was at first supposed that although these dimorphous forms might have the same composition the molecules of

water of crystallization would be combined in different ways, which would become manifest by the rate at which the water is given off. To test this supposition a portion of the tabular barium salt and of the arborescent barium salt were heated in an air bath under the same conditions. Both portions had been powdered to the same degree of fineness. It was found that the loss of water proceeded at the same rate in both forms, thus:

Into crucible A was put .3791 gram Ba salt of the arborescent form.

Into crucible B was put .3834 gram Ba salt of the tabular form.

After heating to 80° for 3 hrs.;

		Percentage of total loss.
Loss in Crucible A	= .0319 gram.	66.87
Loss in Crucible B	= .0320 gram.	66.52

		Percentage of total H_2O
After heating to 118° for 1 hr.:		
Loss in Crucible A =	.0410 gram.	85.95
Loss in Crucible B =	.0375 gram.	77.95
After heating to 140° for 1½ hrs.:		
Loss in Crucible A =	.0464	97.27
Loss in Crucible B =	.0473	98.82
After heating to 180° for 1½ hrs.		
Loss in Crucible A =	.0474	99.37
Loss in Crucible B =	.0476	98.94
After heating to 180-190° for 2½ hrs.		
Loss in Crucible A =	.0477	100.00
Loss in Crucible B =	.0481	100.00

	Calculated for $C_6H_2\begin{Bmatrix}Cl\\COO\\SO_2O\end{Bmatrix}Ba + 3H_2O$	Found. A.	B.
Total loss of H_2O	12.59	12.59	12.55

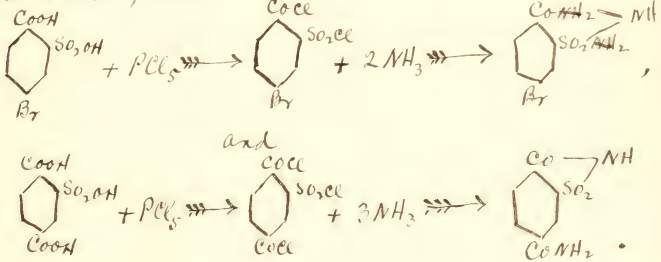
In the row of figures to the right
given the percentage of the loss on any
particular case to the total loss, which is
taken equal to 100.00.

Constitution of p-chlor-m-sulpho-benzoic acid.

As was above stated (p. 19), Cöllen and Bädinger in their work on the p-chlor-sulpho-benzoic acid in question were unable to arrive at any conclusion concerning its constitution.

There are but two possibilities in the case of a mono-sulphonic acid derivative of p-chlor-benzoic acid — the sulphonic acid group may enter into the ortho or the meta relation, relative to the carboxyl group. Now it has been shown in a great number of cases that, when an acid having the carboxyl group and sulphonic acid in the ortho relation is treated successively with phosphorus-penta-chloride and ammonia, the result is always

an imide and not a diamide. In the dicarboxyl acid this tendency toward an imide formation in the ortho relation is most simply illustrated in the case of phthalic acid, which by the treatment above described is converted quantitatively into phthalimide. Cases bearing more directly on a p-chlor-sulpho-benzoic acid, are the conversion of p-brom-o-sulphe benzoic acid into p-brom-sulphinide by Remsen and Bayley[1], and the conversion of ~~ortho~~ sulpho-terephthalic acid into the amide of terephthalic sulphinide by Remsen and Hall[2], i.e.:



(1) Am. Ch. Jr. VIII, 231.
(2) Ibid II, 409.

Therefore if the carboxyl group and the sulphonic acid group are in the ortho relation in this p-chlor-sulpho-benzoic acid, the result of treating it successively with phosphorus pentachloride and ammonia should be p-chlor-benzoic sulphinide , which has been made and studied by J. J. de Roode[1]. The substance which I obtained by treating this p-chlor-sulpho-benzoic acid successively with phosphorus pentachloride and ammonia differs from p-chlor-benzoic sulphinide in all its properties and will be shown to be a diamide (p. 48). Since p-chlor-benzoic sulphinide was not formed and since the diamide is formed, the carboxyl and sulphonic acid groups can not be in the ortho relation, they must be in the meta relation, and the constitution

1) Travis: Some halogen derivatives of benzoic sulphinide. 1890. Johns Hopkins University. p.

of the acid is expressed by

and is p.-chlor-m-sulpho-benzoic acid.

Chlorides of p-chlor-m-sulphobenzoic acid.

The chlorides and amides derived from them were also investigated by Cöllen and Böttinger.[1] The result recorded by them seemed anomalous when compared with the reactions which sulpho-benzoic acids in general undergo when treated with phosphorus pentachloride, and a revision of the work was undertaken.

The chlorides were prepared as follows: The neutral sodium salt, dried at 160° and finely powdered is ground together in

[1] Ber. IX, 1250.

an evaporating dish with an amount of phosphorus pentachloride equivalent to two molecules of phosphorus pentachloride to one of the sodium salt. The reaction takes place spontaneously leaving a whitish oily mass. When this is treated with water, the liquid chloride separates out as a light yellow oil which, on repeated shaking with portions of water, becomes perfectly white and waxen and, on being allowed to stand under water, solidifies after a short time. The solid chloride is then freed from adhering water as well as possible by pressing between folds of filter paper. It is then dissolved in pure anhydrous ether, in which it is very easily soluble, and is freed from a small portion of insoluble inorganic salts which are sometimes still present. If the

ethereal solution is now placed in a large desiccator and the ether is allowed to evaporate off slowly needle-shaped crystals are deposited. They have the general appearance of a pure substance. On determining the melting point, however, it is found that they begin to fuse at 35°, are semi-liquid from 70°-130°, and melt down completely between 130°-155°, the range of the fusing and melting points varying with each preparation. Recrystallization from anhydrous ether did not lead to a substance with a more satisfactory melting point. During the process of crystallization and recrystallization in ethereal solution, fumes of hydrochloric acid were given off which points to a decomposition of the chloride in ethereal solution. In fact a pure

chloride with a sharp melting point which was obtained later on by the use of another solvent underwent change in an ethereal solution. The same chloride could be kept under water for several days without undergoing any very marked change. The use of more than the equivalent of two molecules of phosphorous pentachloride, and heating to 150°, lead to a compound with a tendency to become semi-liquid at a low temperature; the use of the equivalent of one molecule of phosphorous pentachloride and operating at as low a temperature as possible, leads to a compound with a tendency to become semi-liquid at a higher temperature, but these variations in conditions and amount of phosphorous pentachloride did not yield a product

with a fairly limited range in its melting point phenomena.

The crystallized compound melting from 35°–155° is evidently a mixture of chlorides. Its properties agree with those of the mixture obtained by Cöllen and Böttinger, and which they supposed to be a mixture of two mono-chlorides $C_6H_3\begin{cases}Cl\\SO_2Cl\\COOH\end{cases}$ and $C_6H_3\begin{cases}Cl\\SO_2OH\\COCl\end{cases}$.

It is in the first place highly improbable that under the same conditions the carboxyl group would be acted on in one molecule and the sulphonic acid group in another. Furthermore, the chief product of the reaction of ammonia on this mixture is the formation of a diamide $C_6H_3\begin{cases}Cl\\SO_2NH_2\\CONH_2\end{cases}$ (see page 48), which is evidence for the

preponderance of the di chloride $C_6H_3\begin{cases}Cl\\SO_2Cl\\COCl\end{cases}$ in the mixture.

And it was found possible to separate from the mixture of chlorides two distinct chlorides, the one being the dichloride $C_6H_3\begin{cases}Cl\ (4)\\SO_2Cl\ (1)\\COCl\ (1)\end{cases}$ and the other the mono-chloride, $C_6H_3\begin{cases}Cl\ (4)\\SO_2OH\ (1)\\COCl\ (1).\end{cases}$

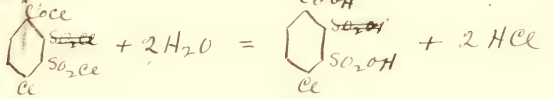
This was accomplished as follows: After the chlorides (prepared as stated on p 3.) had been dissolved in ether to rid them of inorganic impurities, the ethereal solution is rapidly evaporated to dryness by blowing over it with a stream of dry air. In this way small portions of water which were enclosed in the chlorides before dissolving them in ether are gotten rid of. The dry chlorides are then shaken with

succession portions of cold anhydrous ligroine (boiling at 70°-80°), in which the dichloride is rather soluble and the monochloride, insoluble. The solution of the dichloride is concentrated by evaporation in the water-bath, care being taken to avoid the contact of water vapour by placing on the beaker a watch-crystal which just covers the mouth. From the concentrated solution, when cooled slowly, the di-chloride separates in flakes which are nearly pure, by a recrystallization from ligroine are rendered perfectly pure.

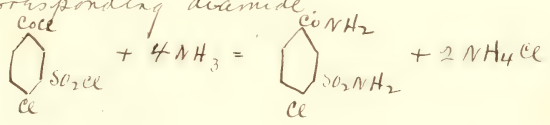
Di-chloride of p. chlor m. sulphe benzoic acid.

This chloride crystallizes from ligroine in flakes with a sharp melting point at 42°-43°. From ether it crystallizes in needles. In

ethereal solution it slowly undergoes change, as is shown by a lowering and indefiniteness of its melting-point. It can be kept under cold water for a considerable time without decomposition, in water at a temperature above its melting point it undergoes rapid decomposition with the formation of p-chlor-m-sulphobenzoic acid:



Treated with ammonia it is converted into the corresponding diamide



A determination of the chlorine was made by boiling the chloride with water containing a little nitric acid. The chloride and water

were boiled in a balloon flask with upright condenser. To avoid any possible loss of hydrochloric acid there was attached to the upper end of the condenser a bent tube which led into a solution of silver nitrate. After boiling for a short time the insoluble chloride is completely decomposed into p-chlor-m-sulpho-benzoic acid and hydrochloric acid according to the equation:

$$C_6H_3\begin{cases}Cl\\COCl\\SO_2Cl\end{cases} + 2H_2O = C_6H_3\begin{cases}Cl\\COOH\\SO_2OH\end{cases} + 2HCl$$

The hydrochloric acid is then precipitated as silver chloride.

An analysis gave the result:

.3442 gram Chloride gave .3525 gram Ag Cl .8534 mm Cl.

	Calculated for $C_6H_3\begin{cases}Cl\\CO\\SO_2\end{cases}\begin{matrix}Cl\\Cl\end{matrix}$	Found
Cl, replaceable by OH	25.93	25.68

Mono-chloride of p-chlor-m-sulpho-benzoic acid.

This chloride is formed in small quantity together with the di-chloride when the sodium salt of p-chlor-m-sulpho benzoic acid is treated with phosphorous pentachloride. It remains undissolved when a mixture of the chlorides is treated with cold ligroine. It crystallizes from ether in needles. It has not yet been obtained in pure condition, as is evident from analyses and from the melting-point which is indefinite between 163° and 167°. Treated with ammonia it yields a very little of the diamide and a soluble salt. The presence of the diamide is accounted for by the impurity of the mono-chloride hitherto obtained, which contains a little of the

di-chloride. The soluble salt formed has not yet been isolated for study.

Determinations of the replaceable chlorine were made as in the case of the di-chloride by boiling with water. Results were obtained as follows:

I. .3142 gram Chloride gave .1797 gram AgCl = .1445 gram Cl.

II. .1520 gram Chloride gave .1003 gram AgCl = gm Cl.

	Calculated for $C_6H_3\begin{cases}Cl\\SO_2OH\\COCl\end{cases}$	Found I	Found II
Chlorine replaceable by H_2O	13.91	14.20	14.27

A determination of the chlorine replaced by the action of ammonia was also made. For this purpose the known weight of chloride is boiled with ammonia in a balloon flask, the chlorine is replaced by ammonia, thus

$$C_6H_3\begin{cases}Cl\\SO_2OH\\COCl\end{cases} + 3NH_3 = C_6H_3\begin{cases}Cl\\SO_2NH_4\\CONH_2\end{cases} + NH_4Cl.$$

after acidifying with nitric acid the chlorine is precipitated as silver chloride. This determination of the replaceable chlorine resulted as follows:

.3886 grm chloride gave .1742 grm $AgCl$ = .1443 grm Cl

	Calculated for $C_6H_3\begin{cases}Cl\\SO_3OH\\COCl\end{cases}$	Found
Chlorine replaceable by NH$_2$	13.91	14.35

In the above analyses the amount of replaceable chlorine found is too high for the mono-chloride. — It is evident that the monochloride melting 154° 157° still contains some di-chloride.

Diamide of
p-chlor-m-sulphe-benzoic acid

By treating the mixture of the chlorides, or the dichloride of p-chlor-m-sulphe--benzoic acid with ammonium hydroxide, the diamide was formed according to the reaction

$$C_6H_3\begin{cases}Cl\\COCl\\SO_2Cl\end{cases} + 4NH_3 = C_6H_3\begin{cases}Cl\\CONH_2\\SO_2NH_2\end{cases} + 2NH_4Cl$$

The diamide was soluble in the excess of ammonia used. For the recovery of the diamide, the solution was evaporated until most of the free ammonia had been given off, and upon acidifying with hydrochloric acid the diamide is precipitated. By washing with cold water the soluble

salts was dissolved away from the insoluble diamide. The amide is readily soluble in hot water and after two recrystallizations separates in excellent needle-shaped crystals which melt at 233°. This diamide has been described by Cöllen and Böttinger as an amide ammonium salt derived from what they supposed to be a mixture of mono-chlorides. It has been shown that this mixture is one consisting mainly of the dichloride which, as could be expected, yields the diamide. The diamide resulting from the mixture of chlorides is far more insoluble than could be expected for an ammonium salt, and does not give off ammonia by treatment with cold caustic soda. The analyses point most clearly to the diamide:

Analysis of Acramide.

I. .2791 gram amide by absolute nitrogen method gave 28.0 c.c's N at 18°. .03294 gram N.

II. .3126 gram amide by Liebig method gave .3094 gram $BaSO_4$ = gram S.

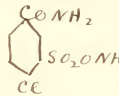
III. .1923 gram amide by Liebig method gave .1914 gram $BaSO_4$ = gram S.

	Calculated for $C_3H_3\begin{cases}Cl\\SCNH_2\\CONH_2\end{cases}$	Found	
		II	III
N	11.97	11.91 (1)	
S	13.66	13.60	13.68

By the Kjeldahl method for nitrogen no results could be obtained. The amide distills out of the sulphuric acid mixture.

(1) .2 % was deducted from the gross result as the allowance for personal error. Fres. Quant. Anal. Ed II, 57.

Amide-ammonium salt and di-anilide.

By treating the monochloride which melts at 164°-167° with ammonia an amide-ammonium salt is formed, which probably has the constitution 

. It is much more soluble than the diamide. It has not yet been obtained in pure condition.

The di-anilide formed by treating the dichloride with aniline was obtained in pure needle-shaped crystals which melt at 219°-220°.

It is the intention of the author to pursue this investigation further, and to

reinvestigate the work done on p-brom-sulpho-benzoic acid, in regard to which, statements analagous to those on p-chlor-sulpho-benzoic acid have been recorded.

The work done thus far and recorded in the foregoing pages leads to the following conclusions:

1st To the volatility of p-chlor-benzoic acid with steam and its occurrence in Commercial Saccharin;

That the action of phosphorus pentachloride on p-sulphamine-benzoic acid is to produce p-chlor-benzoyl chloride and p-chlor-benzo-nitrile; and that the destructive distillation of p-sulphamine-benzoic acid leads to the formation of benzo-nitrile;

That the action of sulphuric acid anhydride on *p*-chlor-benzoic acid is to introduce a sulphonic acid group in the meta position relative to carboxyl, and that the resulting compound is *p*-chlor-*m*-sulpho-benzoic acid;

That the action of phosphorus pentachloride on the sodium salt of this acid is to produce a mixture of the di-chloride and mono-chloride in which the di-chloride is largely preponderant, and not a mixture of mono-chlorides, $C_6H_3\begin{cases}Cl\\SO_2Cl\\COOH\end{cases}$ and $C_6H_3\begin{cases}Cl\\SO_2OH\\COCl\end{cases}$, as recorded by Cöllen and Böttinger;

That the result of treating this mixture of chlorides with ammonia is to produce the di-amide as the chief product and not an amide ammonium salt, $C_6H_3\begin{cases}Cl\\SO_2ONH_4.NH_2\\CO\end{cases}$,

as recorded by Cöller and Böttinger.

In the foregoing pages the following numbers were used as the atomic weights:

For O , 15.96
H , 1.
N , 14.01
Cl , 35.37
S , 31.98
Ba , 136.9
Ag , 107.66
Pb 206.4.

( )

Autobiographical Sketch.

I, Harry Maas Ullmann, was born on the fourteenth day of April, 1868, in Springfield Missouri. My earliest educational training was received in the public schools of that place, upto, which I entered the Central High School at Cleveland, Ohio. I attended the Case School of Applied Science from 1885 to 1887 and in the autumn of 1887 entered the Johns Hopkins University as an undergraduate student in physics and chemistry, graduating with the degree of A.B in June, 1889. Since that time I have pursued post graduate studies at the Johns Hopkins University in Chemistry, Mineralogy, and Physics, under Professors Remsen and Morse, Professor Williams and Professor Kimball, to all

of esteem for their valued interest
and their kindness, I shall always
feel greatly indebted.